

INFLUENCE OF PARTICLE STRUCTURE ON THE RATE OF GAS-SOLID GASIFICATION REACTIONS

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Introduction

Changes in structural parameters, such as surface area available for reaction, porosity, and pore size distribution, will markedly affect the rate of gas-solid reactions. Accompanying these changes in structural parameters are changes in the resistance to diffusion of gaseous products and reactants through the pores of the solid. Understanding the nature of this diffusion, therefore is important in predicting simultaneous diffusion and reaction rates. A quantitative measure of pore diffusion for first-order reactions is given by the effectiveness factor which is a unique function of the effective diffusivity. For microporous solids such as coal, there have been few measurements of effective diffusivity. Furthermore, the effective diffusivity changes as a function of coal conversion as pore walls are gasified. The objective of this work is to determine the changes in the particle structure of coal as it undergoes the reaction, $C + CO_2 \rightarrow 2CO$ and to include the effect of these changes in surface area and effective diffusivity on the overall reaction rate.

A number of workers (1-6) have made measurements of changes in surface area as a function of conversion. Most report that surface area increases during reaction. Only Turkdogan et al (1) and Patel et al (7) have made any measurements of effective diffusivity as a function of conversion. The changes in effective diffusivity, D_e , and total surface area, S , may be expressed as functions of conversion. Once these functions are established, they can be included in an overall rate expression. Recently Bhatia and Perlmutter (8) and Gavali (9) have developed random pore models for gas-solid reactions at chemically controlled rates. These models can be shown to be essentially identical (10). In both cases expressions have been derived which relate surface area to conversion. Bhatia and Perlmutter (11) have extended their model to include diffusion and transport effects where they assume that effective diffusivity will vary with the structural parameters of the solid in the form $D_e = D/\gamma(\epsilon)$ where $\gamma(\epsilon)$ is the tortuosity which varies as reaction proceeds. The random pore models provide a way to interpret rate data in terms of the measurable parameters of surface area and effective diffusivity.

Experimental

The experimental equipment to determine surface and effective diffusivity is the same as used previously (12). The surface area device is a flow-type adsorption apparatus. Surface area measurements were made by adsorbing CO_2 at $0^\circ C$ for 1 hour. The adsorbed CO_2 was then desorbed by heating the sample at $120^\circ C$. This process was repeated at several relative CO_2 pressures to obtain an adsorption isotherm. The surface area was calculated using the Dubinin-Polanyi theory (13) with modifications by Medek (14). Effective diffusivity determinations were made by pulsed chromatography employing the method of moments. The theoretical model used to describe the mass transfer in the chromatographic bed was the same as used previously (12). Axial dispersion and external mass transfer coefficients

were determined from correlations in Shah and Ruthven (15) and Bird (16), respectively. From the two moment equations the adsorption constant K_a and the diffusion parameter D_e/r_c^2 where D_e is effective diffusivity and r_c is diffusion length were calculated. These diffusion studies were made on CO_2 , CO , CH_4 , and N_2 over a temperature range of 50°C to 250°C . To produce char, a sample of raw coal was heated at $25^\circ\text{C}/\text{min}$ to the reaction temperature in a helium gas stream and held at reaction temperature for 1 hour. The sample was cooled and surface area and effective diffusivity measurements were made again. The chars produced were reheated to reaction temperature and reacted with CO_2 . A known volume of CO_2 was injected and the outlet gas was collected and analyzed to determine the extent of the reaction. The sample was then cooled and surface area and effective diffusivity measurements were made. The sample was then reheated and reacted again. This procedure was repeated until there was no further appreciable carbon conversion. Measurements of reaction rates for the char/ CO_2 reaction were made using a thermal gravimetric balance. Devolatilization temperatures and reaction temperatures ranged from 1073K to 1373K.

Results and Discussion

There are significant changes in the surface area and diffusion parameter as a result of devolatilization. Table 1 gives these changes at different devolatilization temperatures. The char surface areas are from 1.5 to 2.0 times as great as the raw coal. The ratio of char/coal surface area increases as devolatilization temperatures increases and reaches a maximum at 1273K and then decreases. The increase in surface area represents the opening of pores inaccessible before devolatilization. Walls closing off pores are devolatilized and small pores inaccessible to initial CO_2 adsorption are exposed. As the devolatilization temperature increases to 1373K the amount of new pores structure begins to decrease as more material is devolatilized. The ratios of the char/coal diffusion parameters for N_2 are less than one indicating that the new pore structure has a greater resistance to diffusion. The ratio of char/coal diffusion parameter increases as devolatilization temperature increases but is still less than one. The devolatilization process produces an increase in surface area and a decrease in diffusion parameter.

The CO_2 /char gasification reaction causes continuous changes in the pore structure of the char. Specific surface area initially increases, passes through a maximum and then decreases as a function of conversion. The specific surface area was correlated with conversion using Bhatia and Perlmutter's expression for surface area as a function of conversion. Figures 1-4 are plots of surface areas versus conversion using the Bhatia and Perlmutter model at each reaction temperature. From the slope and intercept of the least squared line an initial surface area S_0 , and a structural parameter, ψ were calculated. These values along with the measured initial surface areas are given on Figures 1-4. The calculated and measured initial surface areas disagree by as low as 2.5% and as high as 33%. Bhatia and Perlmutter's model indicates that when the structural parameter ψ is greater than 2 that there is a maximum in surface area as a function of conversion. All the values of ψ determined are greater than 2 and the values of ψ increase as a function of reaction temperature up to 1273K and then decrease at a reaction temperature of 1373K. Bhatia and Perlmutter's model has not been widely tested, and the range of conversion over which it applies has not been established. The data of Hashimoto et. al (6) correlated to a conversion of 0.75 for one char and to a conversion of 0.3 for another char. These data correlate from conversion of 0.40 at 1373K to 0.75 at 1173K.

The calculated diffusion parameter, D_e/r_c^2 , and the adsorption equilibrium constant, K_a for the diffusion of carbon dioxide in helium as a function of conversion are displayed in Table 3. The diffusion parameters and equilibrium constants for carbon monoxide, nitrogen and methane as a function of conversion and at different reaction temperature also were calculated but are given elsewhere (17). There is an increase in diffusion parameter with conversion. There appears to be an inverse relationship between the adsorption constant and the diffusion parameter. Intuitively, as the pore structure becomes more open, or as the reactive core decreases in diameter, the resistance of mass transfer decreases.

Walker, et al studied the diffusion of methane in coals and determined that diffusion is activated (18,19). An Arrhenious relationship was proposed to explain the influence of temperature on the diffusion parameter. Activation energies, ΔH_0^\ddagger , and pre-exponential factors, $(D_e/r_c^2)_0$ parameters were calculated from diffusion data obtained at 100°C or greater. The results are listed in Table 6 for char reacted at 1073K. For all gases the activation energy generally decreases with conversion, as expected, since higher energies are associated with smaller pores and pore entrances and with smaller reactive core radii. Patel, et al (7) also observed a decrease in the diffusion of methane through various activated anthracite coals. Activation energies and pre-exponential factors as a function of conversion at the other reaction temperatures are available elsewhere (17). Using calculated activation energies and pre-exponential factors, diffusion parameters were estimated at reaction temperatures. These parameters vary non-linearly with conversion and follow the order $N_2 > CO > CH_4 > CO_2$.

Reaction rate data for char/ CO_2 reaction obtained using the TGA exhibited maxima at intermediate conversions. The Bhatia and Perlmutter model assuming a kinetically controlled reaction and rearranged in linear form was used to interpret the rate data. Values of ψ and S_0 determined from the surface area studies were used in the model. These data are plotted in Figures 5-8. Reaction rate constants were calculated from the slopes of these plots. An Arrhenious plot for the reaction rate constants is given in Figure 9. An activation energy of 150 KJ/mole was calculated from the slope of this plot. The assumption of a kinetically controlled reaction appears to be correct since the reaction rate data in Figures 5-8 are linear as the Bhatia/Perlmutter model suggests and the Arrhenious plot is linear. However, effectiveness factors still need to be calculated and this is currently being done using the Bhatia/Perlmutter model which includes transport effects.

Conclusions

Devolatilization results in an increase in surface area and a decrease in diffusion parameter. A maximum increase in surface area occurs at a devolatilization temperature of 1273K whereas the diffusion parameters increases as devolatilization temperature increases. Specific surface area exhibits a maximum at a conversion of approximately 0.35. The Bhatia/Perlmutter is able to correlate the data to a conversion of at least 0.4. The structural parameter ψ has a maximum at reaction temperature of 1273K. The diffusion parameters, D_e/r_c^2 , are conveniently estimated using the model of Shah and Ruthven (15) and method of moments. The diffusion parameter varies non-linearly with conversion and follows the order $N_2 > CO > CH_4 > CO_2$. The reaction of CO_2 with Wyodak char at temperatures between 1073K and 1373K can be modeled by the Bhatia/Perlmutter model assuming kinetic control. The activation energy is 150 KJ/mole. To confirm this, however, effectiveness factors need to be determined from the simultaneous solution of the equations describing diffusion and reaction including the functions accounting for changes in diffusivity and surface area as a function of conversion.

Acknowledgements

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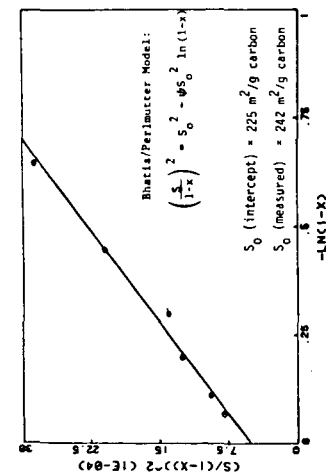


Figure 1. Plot of Bhatia/Perlmutter Model for Surface Area for Wyodak Char Reacted at 800°C $\psi = 7$.

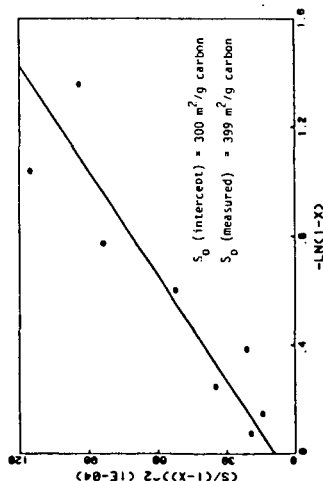


Figure 2. Plot of Bhatia/Perlmutter Model for Surface Area for Wyodak Char Reacted at 900°C $\psi = 8.7$.

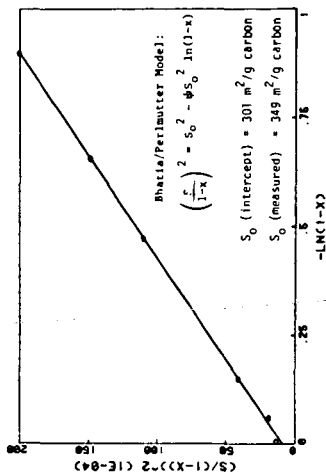


Figure 3. Plot of Bhatia/Perlmutter Model for Surface Area for Wyodak Char Reacted at 1000°C $\psi = 23.6$.

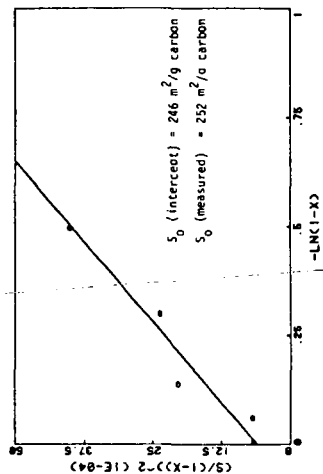


Figure 4. Plot of Bhatia/Perlmutter Model for Surface Area for Wyodak Char Reacted at 1100°C $\psi = 31.2$.

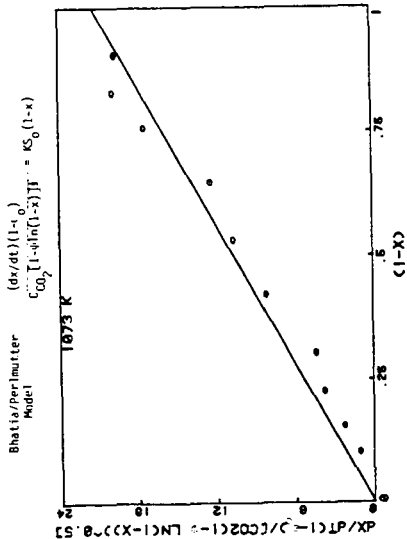


Figure 5. Reaction of Coal Char with Carbon Dioxide at 1073°K. Data fitted to B/P model.

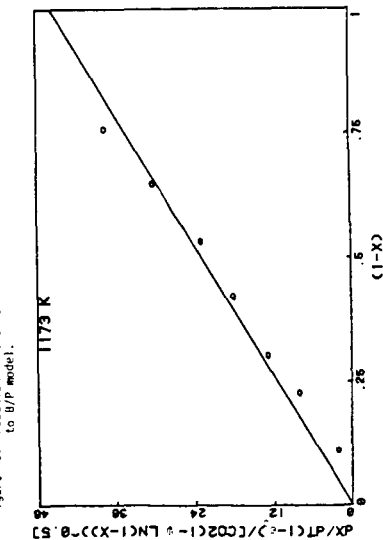


Figure 6. Reaction of Coal Char with Carbon Dioxide at 1173°K. Data fitted to B/P model.

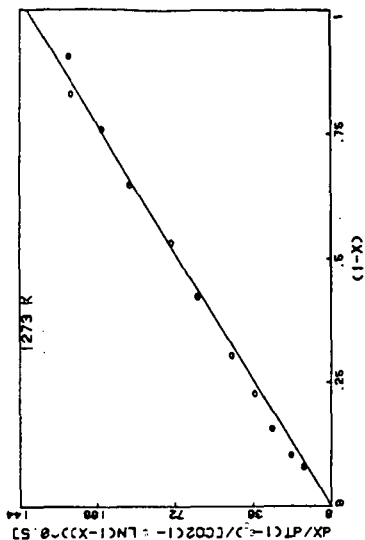


Figure 7. Reaction of Coal Char with Carbon Dioxide at 1273°K. Data fitted to B/P model.

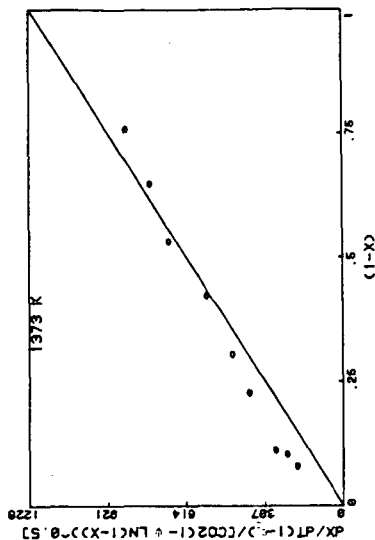


Figure 8. Reaction of Coal Char with Carbon Dioxide at 1373°K. Data fitted to B/P model.

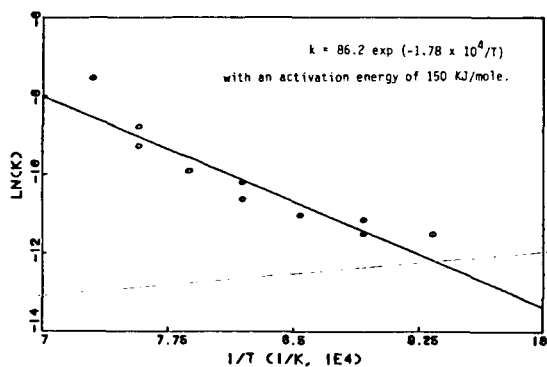


Figure 9. Arrhenius Plot for the Rates Constants.

TABLE 1

EFFECTS OF PYROLYSIS ON WYOMING SUBBITUMINOUS COAL

Pyrolysis Temperature (*K)	Weight (Char/Coal)	Ratio of Specific Area (Char/Coal)	Ratio of H ₂ Diffusion Measured at 323*K (Char/Coal)
1073	.5605	1.81	.234
1173	.5855	1.90	.422
1273	.5749	2.03	.658
1373	.5527	1.47	.708

TABLE 2

WYODAK COAL CHAR REACTED AT 1073°K DIFFUSION PARAMETERS
AND ADSORPTION EQUILIBRIUM CONSTANTS FOR
CARBON DIOXIDE IN HELIUM

Conversion	Adsorption Constant, K_a					Diffusion Parameter, $10^3 D_e/r_c^2$ (s ⁻¹)				
	323°K	373°K	423°K	473°K	523°K	323°K	373°K	423°K	473°K	523°K
0	244	36.7	17.3	11.8	9.79	1.21	5.16	8.36	11.1	12.8
0.061	190	-	19.5	13.1	10.1	1.65	-	5.53	7.79	10.1
0.100	102	-	34.5	11.7	9.74	2.44	-	4.37	7.82	8.57
0.176	94.1	29.3	16.7	10.7	9.11	2.30	5.05	6.02	9.57	10.3
0.247	71.8	23.7	14.4	9.87	8.82	2.73	6.83	6.51	10.6	9.51
0.357	56.7	20.5	11.9	8.88	7.99	3.48	6.08	11.8	13.0	12.4
0.473	41.9	17.8	11.4	8.08	7.36	4.12	6.55	8.53	14.9	15.1
0.583	31.4	15.2	11.0	8.95	7.77	7.64	11.3	12.6	17.3	21.4
0.701	26.1	13.6	-	8.60	-	9.01	13.7	-	21.5	-
0.778	24.1	12.8	8.22	8.71	7.94	11.5	32.0	55.9	48.4	48.1
0.849	34.4	24.3	19.9	11.6	10.4	13.9	54.7	56.5	71.2	64.3
0.865	27.2	25.7	16.2	12.5	11.2	20.4	79.4	74.2	70.3	78.2
0.902	30.3	31.4	17.9	16.0	14.8	25.3	103	80.6	79.0	99.3
0.926	46.9	27.6	19.2	17.1	15.2	52.6	99.3	92.4	105	129

TABLE 3

WYODAK COAL CHAR REACTED AT 1073°K ARRHENIUS PARAMETERS
FOR DIFFUSION OF CARBON DIOXIDE, CARBON
MONOXIDE, NITROGEN, AND METHANE

Conversion	CO ₂		CO		N ₂		CH ₄	
	ΔH_a^\ddagger (KJ/mol)	$(D_e/r_c^2)_0$ (s ⁻¹)	ΔH_a^\ddagger (KJ/mol)	$(D_e/r_c^2)_0$ (s ⁻¹)	ΔH_a^\ddagger (KJ/mol)	$(D_e/r_c^2)_0$ (s ⁻¹)	ΔH_a^\ddagger (KJ/mol)	$(D_e/r_c^2)_0$ (s ⁻¹)
0.0	9.94	0.13	11.0	1.46	9.68	1.09	19.6	8.26
0.061	12.9	0.20	6.18	0.42	5.36	0.35	10.7	1.00
0.100	9.16	0.070	11.2	1.79	6.89	0.57	13.8	2.46
0.176	10.5	0.13	9.84	1.27	6.08	0.48	11.1	1.35
0.247	8.64	0.082	7.29	0.59	5.40	0.36	11.8	1.64
0.357	9.78	0.14	7.15	0.60	5.03	0.34	8.54	0.72
0.473	9.70	0.15	9.88	0.40	4.87	0.32	6.95	0.48
0.583	6.97	0.10	3.34	0.22	4.25	0.28	5.29	0.33
0.701	7.33	0.13	4.69	0.33	4.13	0.29	5.13	0.33
0.778	3.93	0.13	3.32	0.20	2.66	0.18	3.97	0.23
0.849	2.40	0.12	2.84	0.22	3.82	0.28	3.85	0.27
0.865	-	-	3.58	0.26	-	-	6.00	0.45
0.902	3.83	0.24	4.15	0.33	-	-	4.93	0.36
0.926	6.14	0.52	5.15	0.47	5.19	0.48	5.03	0.42